

# LOCAL MAGNETISM OF ISOLATED Mo ATOMS AT SUBSTITUTIONAL AND INTERSTITIAL SITES IN Yb METAL: EXPERIMENT AND THEORY

A.A. Tulapurkar<sup>1</sup>, S.N. Mishra<sup>1</sup>, R.G. Pillay<sup>1</sup>, H.G. Salunke<sup>2</sup>, G.P. Das<sup>2</sup> and S. Cottenier<sup>3</sup>

<sup>1</sup> Department of Nuclear and Atomic Physics, T.I.F.R., Homi Bhabha Road, Mumbai-400005, INDIA.

<sup>2</sup> TP & PE Division, Bhabha Atomic Research Center, Trombay, Mumbai-400085, INDIA.

<sup>3</sup> Instituut voor Kern- en Stralingsfysica, KU Leuven, Celestijnenlaan 200D, B-3001 Leuven, Belgium.

Using TDPAD experiment and local spin density calculations, we have observed large 4d moments on isolated Mo atoms at substitutional and octahedral interstitial lattice sites in Yb metal, showing Curie-Weiss local susceptibility and Korringa like spin relaxation rate. As a surprising feature, despite strong hybridization with the Yb neighbours, interstitial Mo atoms show high moment stability with small Kondo temperature. While, magnetism of Mo, at substitutional site is consistent with Kondo type antiferromagnetic d-sp exchange interaction, we suggest that moment stability at the interstitial site is strongly influenced by ferromagnetic polarization of Yb-4f5d band electrons.

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The formation and stability of local magnetic moments on d-impurities in metallic hosts has been a topic of intense experimental and theoretical investigations over the past several years. While extensive studies have been made for several 3d impurities [1,2], much less information is available on the magnetism of 4d atoms in metals. In general, the d-electrons in 4d metals are regarded as being itinerant and do not show tendency towards local moment formation. Recently, applying time differential perturbed angular distribution/correlation (TDPAD/TDPAC) methods, strong magnetic behaviour has been observed for some substitutional 4d impurities in few metals and alloys [2,3]. The results revealed that, similar to the behaviour observed for 3d impurities, magnetism of 4d ions in metals strongly depends on the type of conduction electrons in the host. Furthermore, it has been argued that moment stability measured by the Kondo temperature,  $T_K$  is strongly influenced by induced spin polarization of host band electrons.

In view of these aspects of magnetism for substitutional 3d and 4d impurities in metals, one can ask : can local moment occur on 3d/4d atoms at interstitial lattice sites also? If so, how stable are the moments? What is the magnitude and sign of host spin polarization and how does it influence the impurity magnetism? Intuitively, due to reduced interatomic distances and the consequent increase in the hybridization strength, one would expect suppressed magnetism for d atoms at interstitial lattice sites. However, large 3d moment has recently been observed for Fe at interstitial sites in fcc Yb metal [4]. Hitherto, magnetism of 4d atoms at interstitial lattice sites in a metal has not been investigated. In this letter we report experimental and theoretical studies on the magnetism of isolated Mo impurity atoms at substitutional and interstitial lattice sites in Yb metal. The results, obtained from TDPAD measurements and local spin density (LSD) calculations show that Mo atoms occupying substitutional and octahedral interstitial sites posses large stable 4d moments with rather small  $T_K$

values. We show that lattice site dependent magnetism of Mo, especially the moment stability, is strongly influenced by the sign and strength of host conduction electron spin polarization.

TDPAD experiments were carried out at the TIFR/BARC Pelletron accelerator facility, Mumbai. We used the  $8^+$  isomer in  $^{94}\text{Mo}$  ( $T_{1/2} = 98\text{ns}$ ,  $g_N = 1.31$ ) as a nuclear probe for the detection of magnetic response. Heavy ion reaction  $^{82}\text{Se}(^{16}\text{O}, 4n)^{94}\text{Mo}$  with pulsed  $^{16}\text{O}$  beam of energy 62 MeV was used to produce and recoil implant the probes in Yb hosts. The estimated concentration of Mo in Yb was less than 1 ppm. Spin rotation spectra,  $R(t)$  were recorded in the temperature range 10 to 300 K by applying magnetic field of 2 T. Further details on the experimental method can be found in Ref. [5]. Measurements were performed in fcc and hcp Yb. Following Ref.[6], fcc Yb could be obtained by rolling a piece of pure (99.9%) metal to a thickness of about 5 to 10 mg/cm<sup>2</sup>. To get the hcp phase, a thin disk of Yb metal was annealed at 400°C for 12 hours followed by repeated cycles of dipping in liquid nitrogen and warming to 300 K. The crystal structures of the samples were verified by X-ray diffraction measurements.

Figure 1 shows some examples of spin rotation spectra,  $R(t)$  for  $^{94}\text{Mo}$  in fcc and hcp Yb along with their Fourier transforms. The spectra show superposition of three frequency components arising from Mo atoms at different lattice sites. They were fitted by the function [5]:  $R(t) = \sum_i A_i \exp(-t/\tau_{N_i}) \sin[2(\omega_{L_i} t - \theta)]$  to extract the amplitude  $A$ , Larmor frequency  $\omega_L$  and the nuclear spin relaxation time  $\tau_N$  of each component. Fig.2 shows the local susceptibilities,  $\chi_{loc}(T) = \beta(T)-1$  of Mo deduced from the relation  $\omega_L(T) = \hbar^{-1} g_N \mu_N B_{ext} \times \beta(T)$ . It can be seen that  $\beta$  for two of the components in fcc as well as hcp Yb, strongly vary with temperature which could be fitted to a Curie-Weiss law:  $\beta(T) - 1 = C/(T + T_K)$ . The Curie constants  $C$  for the two components, in both phases of Yb, were found to be +15(2) K and -32(2) K. Furthermore, the corresponding nuclear relaxation

times  $\tau_N$ , shown in Fig. 3, exhibit Korringa like behaviour ( $\tau_N \propto T$ ). Both these features reflect strong local magnetism of Mo. From the amplitudes ( $A_i$ ), it turns out that nearly 50% of the implanted Mo atoms in fcc as well as hcp Yb show positive Curie constant while a fraction of  $\sim 25\%$  exhibit negative C value. The remaining  $\sim 25\%$  show temperature independent  $\chi_{loc}$  with  $\beta(T) = 1.00 \pm 0.02$ . Tentatively, we assign the components characterized by  $\beta(T) < 1$  and  $\beta(T) > 1$ , respectively to substitutional and octahedral interstitial site. The third fraction ( $\beta(T) = 1$ ) presumably corresponds to a tetrahedral interstitial site. Since fcc and hcp Yb has identical near neighbour environments, for our later discussion of Mo magnetism, we mainly consider the components ascribed to substitutional and octahedral interstitial sites in fcc Yb.

To get theoretical understanding on the lattice site dependent magnetism of Mo in Yb host, we have performed first-principles spin polarized, semi-relativistic supercell electronic structure calculations within local spin density approximation (LSDA), employing tight binding linear muffin-tin orbital method in atomic sphere approximation (TB-LMTO-ASA) [7] and Von-Barth-Hedin [8] parameterization for the exchange correlation potential. Calculations were carried out for a single Mo impurity at substitutional as well as octahedral interstitial site, using cubic supercells (space group Pm3m) of dimension twice the lattice constant of fcc Yb, with 32 (33 for interstitial case) atoms and treating Yb-4f as band electrons. In order to accommodate the large Mo impurity in the interstitial site without violating the overlap criterion prescribed by ASA, the nearest neighbour (nn) Yb atoms had to be relaxed outwards by at least 5% of the nn distance. The next nearest neighbour atoms were left unrelaxed thus keeping the unit cell volume intact. No relaxation was necessary for treating the substitutional case.

Figure 4 show the up and down spin local density of states (LDOS) of Mo-d electron. The results showing large splitting of the two spin sub bands clearly indicate the presence of high local 4d moments on Mo. The calculated moments, summarized in Table I, turn out to be  $3.56\mu_B$  for substitutional and  $1.12\mu_B$  for the interstitial Mo atoms. For further confirmation of the rather high moment of Mo, especially at the interstitial site, we performed additional calculations using spin polarized full-potential linearized augmented plane wave (FLAPW) method as implemented in WIEN code [9]. The resulting Mo moments  $3.21\mu_B$  for substitutional and  $1.29\mu_B$  for the interstitial sites closely agree with the LMTO-ASA results. For the interstitial case, calculations with higher lattice relaxation, 17% taken from assumption of hard sphere atomic radii, yielded larger moment  $\sim 1.8\mu_B$  ( $2.1\mu_B$  from FLAPW method).

Coming back to the experimental results, the Mo magnetic moments can be estimated from the Curie con-

stants using  $C = g(S+1)\mu_B B(0)/3k_B$  [5] where  $B(0)$  is the hyperfine field at 0K. For half filled 4d-shell, neglecting orbital contribution, the measured  $B(0)$  consists of a negative core polarization field,  $B_{CP}$  and a positive term ( $B_{val}$ ) arising from the valence electrons. The net spin contact hyperfine fields for many 4d impurities have been found to lie between -200 kG and -280 kG [10]. Assuming  $B(0) = -240$  kG, the Mo moment for the minority fraction ( $\beta(T) < 1$ ) turned out to be  $3.96\mu_B$  which is close to the value calculated for substitutional site. This supports our earlier attribution of the  $\beta(T) < 1$  component to Mo atoms at substitutional lattice site. For the majority fraction, the observed  $\beta(T) > 1$  behaviour implies  $B(0)$  to be positive which can arise from a larger contribution from the valence 5s electrons and much reduced value of  $B_{CP}$ . The exact value of  $B(0)$  though difficult to calculate, one can get a reasonable estimate from the  $\tau_N$  data [11] which came out to be  $\sim +19 \pm (2)$  T. With this  $B(0)$ , the Mo moment for majority fraction was found to be  $1.5 \pm 0.3\mu_B$ , in accordance with the values calculated for octahedral interstitial site. This gives credence to our assumption that the component with  $\beta(T) > 1$  arises from Mo atoms at octahedral interstitial site. The above site assignment is also supported from results reported for Fe in Yb [4]. Here, we like to emphasize that any uncertainty in  $B(0)$  and the consequent spread in the Mo moments does not influence the main conclusions of this work.

We now examine the stability of Mo magnetic moments in Yb which can be scaled with the Kondo temperature,  $T_K$ . The later can be derived from the Curie-Weiss fit of  $\beta(T)$  data. The measured  $\beta(T)$  corresponding to substitutional as well as interstitial sites in fcc Yb yielded  $T_K = 60 \pm 10$  K. For Mo in hcp Yb the  $T_K$  values for the two sites were found to be  $35 \pm 5$  K. An estimation of  $T_K$  could also be obtained from the spin relaxation rates  $\tau_J$  extracted from the  $\tau_N$  data [11,12]. The  $T_K$  derived from  $\tau_N$  data again turn out to be similar for both substitutional and interstitial sites, being  $\sim 55$  K for fcc Yb and  $\sim 20$  K for hcp Yb. The  $\beta(T)$  and  $\tau_N$  results indicate rather high moment stability for Mo at substitutional as well as interstitial lattice sites.

Finally, by analyzing the Kondo temperatures of site specific Mo moments in Yb we show that magnetism, particularly moment stability, is strongly influenced by the sign and strength of spin polarization of host conduction band electrons. Starting from Kondo model, instability of a magnetic moment is caused by antiferromagnetic exchange interaction between impurity-d and host conduction electrons. The degree of instability proportional to  $T_K$  is governed mainly by the Kondo resonance width [12]  $\Gamma = \pi N(E_F)V_{kd}^2$ , where  $V_{kd}$  is the hybridization strength. For divalent Yb with dominantly sp type conduction electrons, the hybridization strength can be roughly estimated using the procedure given in Ref [13] and are listed in Table I. Using these  $V_{kd}$  values

the  $T_K (= \Gamma/k_B)$  of substitutional Mo impurity in fcc Yb was found to be  $\sim 75$  K in close agreement with the value 60 K measured experimentally. Further more, the magnetism of substitutional Mo atom in Yb is consistent with the trend observed in alkali and alkaline earth metals [11,14] where by the reduction in moment correlates with the hybridization strength. The above analysis show that magnetism of substitutional Mo in Yb can be well understood within Kondo model. Extrapolating the same physical picture to Mo impurity at interstitial site, due to stronger hybridization strength (see Table I) one would expect the moment to be highly unstable with  $T_K > 400K$  leading close to nonmagnetic behaviour with  $\beta(T) = 1$ . Instead, interstitial Mo atoms in Yb show rather stable moment with Curie-Weiss type  $\beta(T)$  and a low  $T_K \leq 60$  K.

What is the physical reason for the high moment stability of interstitial Mo atom in Yb? To understand this, we look into the host spin polarization by examining the induced moments at the Yb sites. The results listed in Table I clearly reveal that sign and strength of host polarization for the interstitial site qualitatively differ from the features seen for substitutional case. For substitutional Mo, the small negative moment at Yb site, mainly arising from sp-band electrons, implies an antiferromagnetic polarization of host band electrons. In contrast, Yb atoms surrounding the interstitial Mo impurity show substantial positive moment largely due to ferromagnetic polarization of 4f5d band electrons of Yb. From the results presented above, we believe that this induced ferromagnetic polarization causing strong interatomic interaction between Mo-4d and host conduction electrons is mainly responsible for the high moment stability of interstitial Mo atoms in Yb. The features of host polarization found for interstitial Mo in Yb and its influence on  $T_K$  show striking similarity with the results observed for 3d, 4d impurities in some d band metals viz. Pd and PdFe alloys [3,15,16]. As a plausible mechanism, we suggest that interatomic ferromagnetic interaction between Mo-4d and host conduction band electrons can compete and successfully suppress  $T_K$  arising from antiferromagnetic d-sp exchange interaction and thereby stabilize the magnetic moment of Mo at the interstitial lattice site. The above physical picture is consistent with prediction of recent theoretical calculations where a ferromagnetic interaction between the impurity and host conduction electrons has been shown to suppress the Kondo resonance at Fermi energy [17].

To conclude, combining TDPAD experiments with local spin density calculations, large 4d local moments have been observed for Mo atoms at substitutional and octahedral interstitial lattice sites of fcc and hcp Yb metal. While, the magnetism of Mo, for the substitutional site is consistent with Kondo type antiferromagnetic d-sp exchange interaction, we find that magnetism and Kondo temperature of interstitial Mo atom is

strongly influenced by ferromagnetic polarization of host Yb-4f5d band electrons. The results and interpretations presented in this letter provide an important basis for understanding local magnetism of interstitial d-impurities in a metallic host. They also yield insight on the key role of host polarization on the occurrence and stability of local moments in general.

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FIG. 1.

Spin rotation spectra,  $R(t)$  (left panel) and their Fourier transforms (right panel) for  $^{94}\text{Mo}$  in fcc and hcp Yb.

FIG. 2.

Local susceptibility  $\beta(T)$  of Mo in fcc (filled symbols) and hcp (open symbols) Yb as a function of  $1/T$ . The solid lines correspond to fits by Curie-Weiss law:  $\beta(T) - 1 = C/(T + T_K)$ .

FIG. 3.

Nuclear relaxation time  $\tau_N$  as a function of temperature for  $^{94}\text{Mo}$  in fcc Yb (filled symbols) and hcp Yb (open symbols). The linear dependence of  $\tau_N$  with  $T$  (solid lines) is indicative of Korringa like relaxation process (see text).

FIG. 4.

Local density of states (LDOS) for a Mo impurity in fcc Yb host occupying substitutional and relaxed (5%) octahedral interstitial sites.

TABLE I.

Summary of Kondo temperature  $T_K$ , hybridization strength  $V_{kd}$  and calculated (LMTO method) magnetic moments,  $m_0$  for a Mo impurity at substitutional and relaxed (5% and 17%) octahedral interstitial lattice sites in fcc Yb.  $m_1$  and  $m_2$  are the induced moments at nearest and next nearest Yb atoms.

	<i>Substitutional</i>	<i>Interstitial</i>
$T_K(\text{K})$	60	60
$V_{kd}(\text{eV})$	0.104	0.256
$m_0(\mu_B)$	3.56	1.12(1.77 <sup>+</sup> )
$m_1(\mu_B)$	-0.013	0.12(0.29 <sup>+</sup> )
$m_2(\mu_B)$	0.008	0.0(0.06 <sup>+</sup> )

+ correspond to results obtained with 17% lattice relaxation.

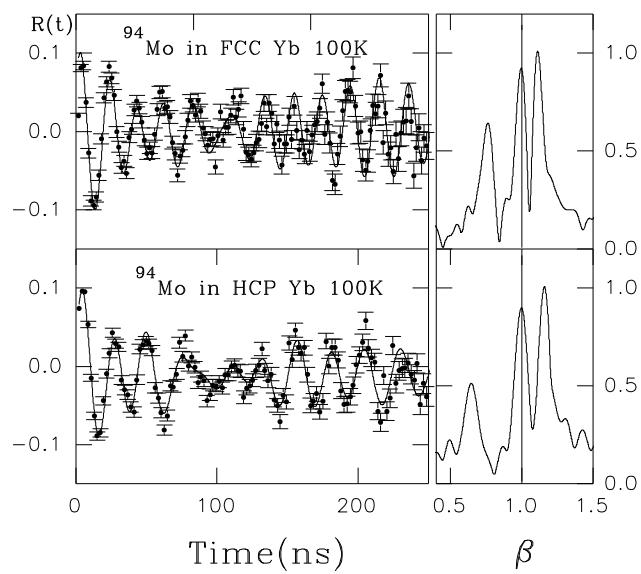


Fig.1 Tulapurkar et al. LE7408 (revised manuscript)

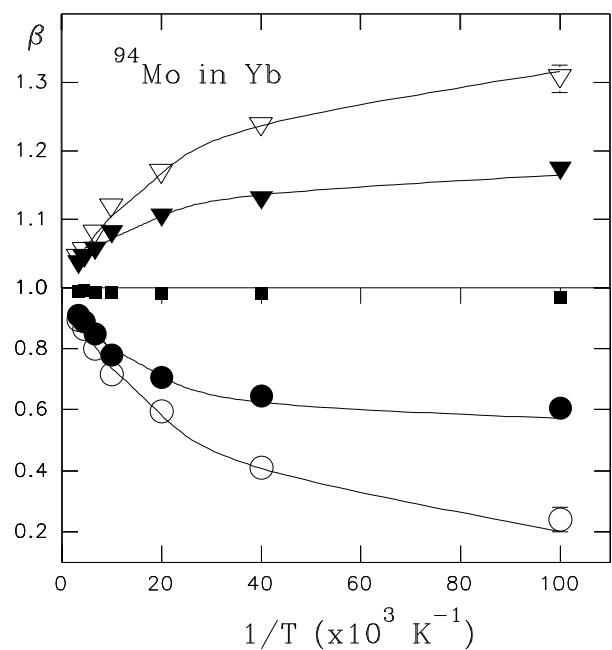


Fig. 2 Tulapurkar et al. LE7408 (revised manuscript)

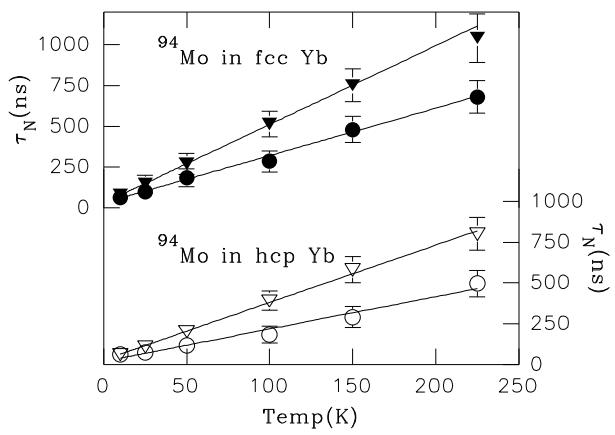


Figure 3. Tulapurkar et al. LE7408 (revised manuscript)

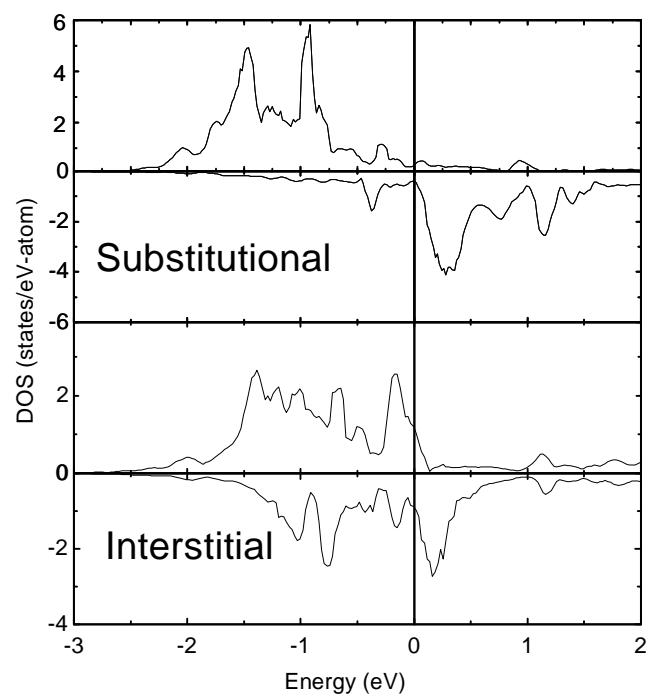


Fig.4 Tulapurkar et al. LE7408 (revised manuscript)